# A Comparison between Corn Starch and Dry Milled Corn Products in their Dispersion Properties

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Gelatinization of corn starch, flour, meal and grits has been compared. Amylograph curves show differences that can be related to particle size and to constraints on the swelling behavior, presumably due to native protein in the corn milled products. Autoclaving starch and dry milled products at 121°C in the presence of steam alone merely hardens the particles. However, when the particles are in contact with liquid water, swelling and gelatinization readily occur and gels are formed. Above 10% loading, gels formed by autoclaved grits and meal are significantly more rigid than gels formed from corn starch alone. Flour gives gels of essentially the same properties as the starch up to 30% loading, above which flour gels become more rigid than starch gels and match the gels formed from corn meal and grits.

**Ein Vergleich zwischen Maisstärke und trocken vermahlenen Maisprodukten hinsichtlich ihrer Dispersionseigenschaften.** Die Verkleisterung von Maisstärke, Maismehl, Maisschrot und -grits wurde verglichen. Die Amylogramme zeigen Unterschiede, die auf die Teilchengröße sowie auf die durch natives Protein in den Maismahlprodukten auftretenden, das Quellverhalten beeinflussenden Hemmungen zurückgeführt werden können. Die Autoklavbehandlung von Stärke und Trockenvermahlungsprodukten bei 121°C in Gegenwart von Dampf allein verhärtet lediglich die Teilchen. Wenn die Teilchen jedoch mit flüssigem Wasser in Berührung kommen, so tritt ohne weiteres Quellung und Verkleisterung auf, und es bilden sich Gele. Oberhalb einer Konzentration von 10% sind die aus autoklavbehandelten Grits und Schroten gebildeten Gele fester als die allein aus Stärke gebildeten. Mehl ergibt Gele von im wesentlichen gleichen Eigenschaften wie Stärke bis zu 30%. Oberhalb dieser Konzentration sind Mehlgele fester als Stärkegele und entsprechen den aus Maisschrot und -grits gebildeten Gelen.

## 1 Introduction

Rheological and mechanical properties of starch-water dispersions and gels wherein essentially pure starch has been swollen and/or solubilized to various extents by heating have been extensively investigated over the years [1–4]. These studies have contributed to an understanding of the gelatinization mechanism and are important because of the utilization of starch in a wide range of food and industrial applications (or products). As *Sterling* [5] stated in his excellent review "... understanding these properties offers considerable promise in improving starch containing foods", this knowledge can be applied to alter end use properties by reformulation or changes in processing conditions.

The emphasis in the literature has been on the behavior of starches, particularly those starches of great economic importance such as wheat and corn. Relatively little has been published on the behavior of starches that remain associated with native protein. Studies detailing the modification of cereal flours for some industrial uses have been reported from this Center [6, 7, 8, 9]. Nevertheless, the behavior of dry milled products such as corn grits, meal and flour has not been directly compared to our knowledge in the literature with pure starch behavior. In some applications a direct substitution of a corn or wheat flour for corn or wheat starch can be made and comparable products resulted, as discussed by *Fanta* et al. [10] in reference to starch graft absorbent polymer. There were minor differences, such as for example, a higher percentage of polymer being extractable with dimethyl formamide from the grafted corn flour than from the grafted starch.

The purpose of this study is to explore some of the physical differences between corn starch and dry milled products. This study includes a comparison of the amylograph response of starch and dry milled products and a comparison of the elastic moduli of gels formed by autoclaving starch and dry milled products in the presence of liquid water.

## 2 Experimental

### Materials and Methods

#### Materials

Grits for the autoclaving studies were obtained from yellow dent degermed corn (Lauhoff Grain Co., Danville, IL). These had a protein content of 9.0% (d. b.) and a moisture level of 12.2%. For the amylograph studies commercial streams of dry milled corn products were obtained from Krause Milling Co., Milwaukee, WI. Medium grits = 8.9% (d. b.) protein, 11.6% moisture; corn meal = 7.7% (d. b.) protein, 12.6% moisture; corn flour = 7.0% (d. b.) protein, 11.7% moisture. Starch used was a commercial grade having 0.3–0.4% protein and 11.4% moisture.

#### Sample preparation

A "flour" was pin-milled from the Lauhoff grits by three successive passes (Alpine 160Z; 14,000 r. p. m.) so that 75.3% by wt. passed a 6XX cloth (Protein = 8.7% (d. b.) moisture = 9.75%). A meal product (−50 + 6XX) was screened from this material (Protein = 9.9% (d. b.), moisture = 9.8%). A portion of the original grits was tempered to 25% moisture, spread 7–10 mm deep on foil and steamed in an autoclave (AMSCO 57CR) at 121 ± 3°C for 120 min. The product was cooled to 90–95°C before opening the chamber, and the moisture determined for Amylograph measurements. In addition, water dispersions of grits, flour and starch containing 10–44% total solids were autoclaved for 120 min at 121°C. This period includes about 20 min needed for the dispersions to attain chamber temperature. It was necessary to first slightly thicken the dispersions (boiling water bath) before autoclaving to prevent settling. On removal from the chamber they invariably had a "skin" present which easily lifted away before ladling

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into 76 mm dia. × 12 mm PVC molds. 100 mm × 100 mm Lucite squares covered with Saran were clamped down to squeeze out excess material and to close the molds. The gels were left clamped to stand at room temperature (21–23°C) for 20–26 h before measurement.

### Amylograph measurements

A Brabender VAV1 instrument, with 700 cm-g sensitivity, was calibrated and adjusted to a standard starch (C. W. Brabender Inc., South Hackensack, NJ). With steamed grits the total solids were all at 9.0 wt. %. With unsteamed grits, meal, flour and starch the solids were adjusted to 8.2% starch content. pH = 6.7–6.9. The cycle used was: heat to 95°C, hold at 95°C for 16 min, cool to 50°C. Heating and cooling rates were 1.45–1.5°C per min.

### Mechanical spectrometer measurements

A Rheometrics Model KMS-71 was used for measuring a shear modulus and two dynamic moduli with the same test material in the instrument. This was permissible since the strains employed were small. All measurements are at 20–22°C. For measurement, the dispersion was gently removed from the mold and bonded to the upper and lower platens with cyanoacrylate ester adhesive [11]. It was then allowed to stand 5–15 min until the stresses introduced during loading relaxed to a constant value. A chamber lined with wetted filter paper surrounded the platen/gel assembly to retard drying of the trimmed edge. The principle and operation of the instrument have been described elsewhere [12–13]. In measuring the simple shear modulus, the lower platen is displaced with respect to the upper platen in 0.002 mm increments to a total displacement of 0.010 mm. These displacements are sufficiently small to maintain linearity between stress and strain. The resisting force Fy is recorded at each displacement. The shear modulus equals **(1)**:

$$G = \frac{(Fy)(g)(h)}{\pi r^2 a} \text{ dynes/cm}^2 \quad \textbf{(1)}$$

where $Fy$ = grams force, $g$ = 981 dynes per gram force, $h$ = sample thickness (cm), $r$ = sample radius (3.6 cm), $a$ = displacement (cm).
The storage (elastic) and loss (viscous) moduli were determined by dynamic stressing with the assembly rotating at an angular velocity (ω) of 10 or 70 radians per second. The lower platen was displaced to a total of 0.050 mm at each angular velocity. This small displacement assured that linearity was maintained. The storage modulus $G'$ and loss modulus $G''$ were calculated as **(2)** und **(3)**:

$$G' = \frac{(Fy)(g)(h)}{\pi r^2 a} \text{ dynes/cm}^2 \quad \textbf{(2)}$$

$$G'' = \frac{(F_x)(g)(h)}{\pi r^2 a} \text{ dynes/cm}^2 \quad \textbf{(3)}$$

The calculated valus were corrected for instrument compliance [12] when they were greater than $1 \times 10^5$ dynes/cm$^2$. This was accomplished by computer program on a MODCOMP CLASSIC 7870.
The solids content of the dispersions was determined on removal from the platens by drying the sample for at least 6 h at 120°C in an air circulating oven.

## 3 Results and Discussion

### 3.1 Amylograph Response

Figure 1 shows the amylograph response for corn grits, meal and flour at 9% total solids corresponding to a starch level of 8.2% by weight. For comparison two amylograph curves for corn starch are shown. One curve, 9.0% corn starch, is for the same total solids level as for the dry milled products; the second is for 8.2% corn starch corresponding to the starch level in the dry milled product dispersions. The two starch curves show a first perceptible rise in torque around 68°C and a steep rise to 300 BU in the range 74–79°C.
In contrast, the flour curve rises less steeply to this 300 BU value but over a much lower temperature range, about 68–75°C. This rise occurs at lower temperatures for the flour than the starch presumably because of starch damage occurring during milling of the flour. This damage will increase both solubilization of starch and the ability of the starch to swell. Above this torque level, the constraint of the native protein on the starch swelling in the flour is evident and the maximum torque level reached with the flour is only 50% of the starch response.
The flour particle sizes are larger than for the starch granules alone and this will influence the swelling rate, thereby increasing the time to attain full swelling equilibrium. As heating proceeds the curve for corn flour has a broad peak, with a maximum of 480 BU at 86°C. After reaching the maximum, the torque level for the flour curve decreases and during the hold period falls to a value of 370 BU, a decrease of 110 BU from the peak. During this period the starch dispersions decreased by 205 and approximately 250 BU from peak levels for the 8.2 and 9.0% concentration, respectively. During the hold period the decrease in torque for starch samples is usually attributed to granule breakup and solubilization of starch molecules [14–15]. It is worth noting that although the magnitude of the decrease in torque during the hold period is larger for starch

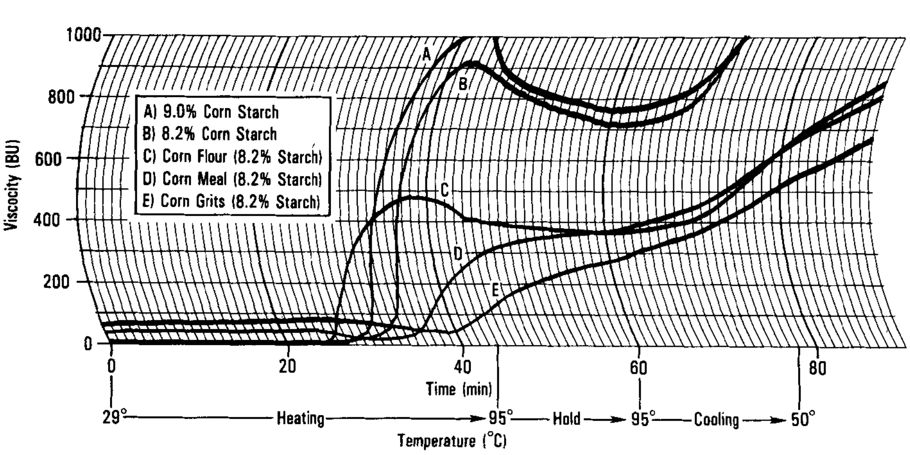


Figure 1. Amylographs of corn starch and dry milled corn products. Solids concentrations: A = 9.0% corn starch; B = 8.2% corn starch; C = corn flour, 9.0% total solids (8.2% starch); D = corn meal, 9.0% total solids (8.2% starch); E = corn grits, 9.0% total solids (8.2% starch).

than for flour, the percent change from the peak height is the same, 23%. On this basis there appears to be little difference in the behavior of the starch and flour during the hold at 95°C.

From 29°C to about 62°C the torque for the corn meal slurry is significantly higher (40 BU) than for the starches and flour. At about 62°C the curve has a slight rise, probably due to damaged starch, followed by a decrease to a broad minimum occurring at 74°C. The torque then rises but increases less rapidly than for flour to the 95°C hold period during which period it continues to rise. The corn meal particles are significantly larger than the corn flour and obviously retain a rigid core longer than the flour. The swelling is a slow process and continues during the hold period, resulting in the observed continual increase in torque reading.

With the still larger grit particles the torque level in the initial temperature range is significantly higher than for either corn starch, flour or meal. In addition the trace is a wide band with a slight maximum around 65°C. The torque then decreases somewhat, the band width narrows and a minimum is observed near 87.5°C. The initial wide band response is probably due to the fact that grit particle sizes are comparable to the machine gaps through which they pass. The decrease in band width results from softening of the particles. The torque reading then increases continuously, even during the hold period, but at a slower rate than meal (or flour). The actual levels are appreciably lower than for the meal or flour. The swelling and solubilization processes for these large grit particles are very slow and it is evident that there is no equilibrium in either swelling or solubilization during the time scale of these measurements.

The conclusions we reach from these amylograph curves are as follows: The fact that the flour response is less in magnitude than that of starch after swelling begins, and the rate of rise is less, can be attributed to the swelling being constrained by the associated protein. Particle size differences will also influence the swelling rate since the larger the particle, the longer it will take the water to penetrate to the center. As long as this center remains dry and rigid, unplasticized by water, the swelling of the outer portions will be constrained. The fact that the flour shows a torque rise at lower temperatures than the starch is attributable to starch damage during the flour milling process.

With corn meal, being of still larger particle size, diffusion to the granule center will take even longer, and with less starch damage presumably, the amylogram shifts to higher temperatures with a lower slope since attainment of swelling equilibrium is slower. Furthermore, swelling is far from complete by the time 95°C is reached so the swelling continues during this portion of the process. These particles also are less susceptible to mechanical damage in the amylograph than flour or starch, especially during the hold period.

For the large grits the process is primarily controlled by the diffusion rate of the water into the granule.

As expected, the properties of corn milled products, though the particles consist primarily of starch, show strikingly different amylograph responses compared to starch, which must be directly related to particle size, where the unswollen central core constrains the swelling of the outer portions of the particle and to the protein which also will slow diffusion and constrain swelling.

### 3.2 Autoclaving Studies

It had been established in the literature that autoclaving starch, (*Sair*, [16]), or dry milled corn products, (*Peplinski* and *Pfeifer* [17]) in an atmosphere of steam serves merely to harden the granules. This was surprising to us since the water activity is such that granule swelling and starch solubilization would be expected to occur. This happens, for example, if sugar is placed in an autoclave under the same conditions. The sugar will absorb water, dissolve and form very concentrated solutions very readily. Nevertheless, in carrying out the experiments with starch and grits we obtained exactly the same results as reported in the literature, even though our steaming time was extended to 120 min. Particle hardening occurred as reflected in the much reduced amylograph response shown, for example, by *Peplinski* and *Pfeifer* [17] and which we confirm in our study. Since steaming did not form gels, experiments were next carried out by placing the granules in liquid water for autoclaving.

Although the water activity under the autoclaving conditions (121°C) was presumably the same as without the liquid water initially present, the response of the granules was quite different. They swelled extensively and when removed from the autoclave it was apparent that gels had formed. The gels were not homogeneous but showed the highly swollen granules still discernible and suspended in the gels. In the initial experiment with the granules covered by water resting on the bottom of the container, a concentration gradient was evident, with the highest concentration of swollen particles on the bottom and decreasing concentration towards the surface of the liquid water. Subsequently, in preparing gels under autoclaving conditions, the granules were preswollen to a level which inhibited particle settling in the suspending medium and were then placed in the autoclave for final gel preparation. The mechanical properties of these gels were then examined.

We conclude that the liquid phase water must be present during autoclaving of starch and corn dry milled products to provide a sink into which solubilized starch (initially amylose) can exit from the granule.

### 3.3 Rheological Properties of Autoclaved Gels

Figure 2 shows the response of 20.0% gels of corn grits and of corn starch autoclaved for 120 min at 121°C. In this figure the measured force (in g) is plotted against strain, $\varepsilon = a/h$, where $h$ is the sample height and $a$ the horizontal displacement of the initially coincident axes of the upper and lower plates. The response is linear.

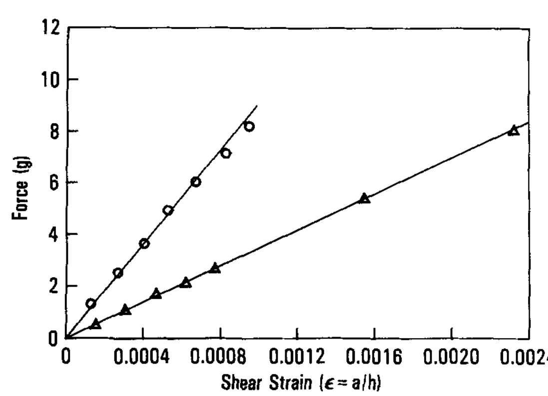


Figure 2. Force *versus* strain in simple shear for corn grits and corn starch dispersions gelled in the presence of liquid water in an autoclave at 121°C for 120 min. Solids 35.0% by wt., measurements made at 22°C. Sample radius = 3.6 cm, nominal height = 1.1 cm; ○ = grits, △ = starch.

Figure 3 compares the modulus, $G$, obtained in simple shear as a function of gel concentration for corn starch, grits and flour (pin milled from the grits). The concentrations were determined on the samples after the experiment. The materials are equivalent up to the 10% level but above this concentration the moduli for starch and flour start to fall below the values for the

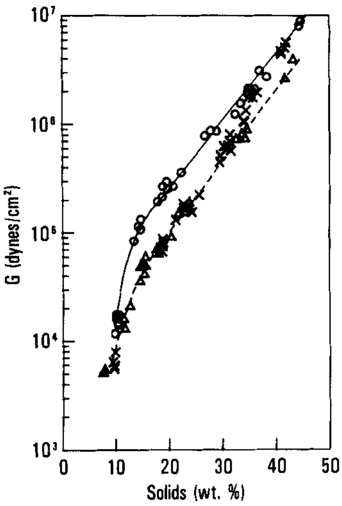


Figure 3. Effect of total solids concentration on the modulus ($G$) determined in simple shear. Materials autoclaved for 120 min at 121°C, measurements at 22°C. Nominal sample dimensions as for Figure 2; ○ = corn grits, △ = corn starch, × = corn flour.

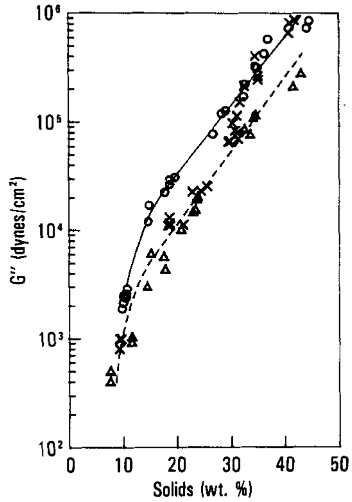


Figure 5. Effect of total solids concentration on the dynamic loss modulus, $G''$. Preparation conditions and dimensions as for Figure 4. $\omega = 10$ radians/s; ○ = corn grits, △ = corn starch, × = corn flour; measurements at 22°C.

grits. At about 30% the flour gel results diverge from the starch response and approach the curve for the grits.

The observation that the grits give a larger modulus at the same concentration as the starch is reasonable from visual examination of the gels. The cores of the swollen grits are very evident and these partially swollen and relatively rigid cores undoubtedly serve as reinforcing filler in the gel. The gel itself, based on a qualitative iodine test, is obviously an amylose system. The amylose has diffused from the grits into the suspending water and is the primary agent for gel formation.

The storage modulus ($G'$) and loss modulus ($G''$) for these systems obtained in the eccentric rotating disc mode, are shown in Figures 4 and 5. The G' values are very close numerically to the simple shear modulus G.

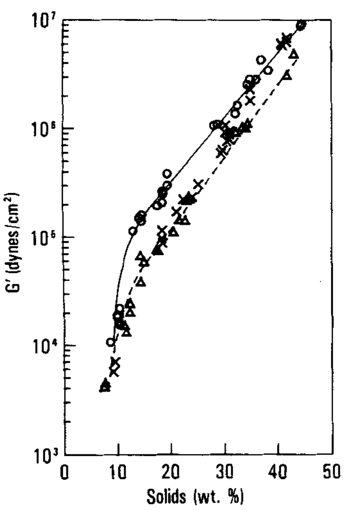


Figure 4. Effect of total solids concentration on the dynamic storage modulus, $G'$. Preparation conditions and dimensions as for Figure 3. $\omega = 10$ radians/s, measurement at 22°C; ○ = corn grits, △ = corn starch, × = corn flour.

The values of $G'$ were found to increase by only about 14% as the frequency is increased from 10 to 70 radians/seconds. Values of $G''$ however show a greater frequency dependency increasing by 41% for the grits and 67% for the flour preparations in going from 10 to 70 sec$^{-1}$ (for clarity only the results at $\omega = 10$ are shown in Fig. 5). The absolute values of $G''$ are approximately one decade below the corresponding $G'$ values.

The same pattern is observed in the dynamic measurements as was seen in simple shear. The moduli for grits are about 2 or 3 times those for starch. The flour matches starch at concentrations between 10 and 30% but approach grits at higher concentration. The only additional information given by the dynamic results is the frequency dependence of $G''$.

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